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APPLICATION

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TITLE: METHOD FOR FORMING AN ARRANGEMENT OF BARRIER LAYERS ON A POLYMERIC SUBSTRATE

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METHOD FOR FORMING AN ARRANGEMENT OF BARRIER LAYERS ON A POLYMERIC SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to European Patent Application No. 03005270.8, filed on March 10, 2003, which is incorporated by reference herein.

BACKGROUND

Many products, for example food, electronic devices and pharmaceuticals, are very sensitive to moisture and oxidizing agents. Many of these products rapidly degrade when exposed to water, oxidizing agents or other gases or liquids. Polymeric substrates, such as polymeric foils, are often used to package these products. These foils frequently exhibit a permeability for water vapor and for oxidizing agents in the range of more than $1 g/(m^2 * day)$. This high degree of permeability is unacceptable for most of the products packaged in polymer foils.

One packaging application that uses polymeric substances is the packaging of organic electroluminescent devices (OLEDs). An OLED device includes a functional stack formed on a substrate. The functional stack includes at least one organic functional layer sandwiched between two conductive layers. The conductive layers serve as electrodes (cathode and anode). When a voltage is applied to the electrodes, charge carriers are injected through these electrodes into the functional layers and upon recombination of the charge carriers, visible radiation can be emitted (electroluminescence). The functional stack of the OLED is very sensitive to moisture and oxidizing agents, which can cause oxidation of the metals of the electrodes or deterioration of the organic functional layers. The next generation of organic electroluminescent devices are likely to be arranged on flexible substrates, such as polymeric substrates, and are under current investigation. For a sufficient OLED lifetime, polymeric substrates with a permeability for water or oxidizing agents below $10^{-6} g/(m^2 day)$ are desirable.

Patent application WO 00/48749 A1 describes a method of reinforcing polymeric foils with thin ceramic barrier layers in order to block out gases or liquids more efficiently than when only polymeric foils are used. Ceramic layers frequently have

defects in their microstructures that can serve as continuous paths for gases and water vapor to pass through the ceramic barrier layers. These defects lead to a decreased ability of the ceramic barrier layers to serve as a barrier. In this context, all pathways through the inorganic, ceramic barrier layers are called defects. Defects in the context of this specification include pinholes, grain boundaries, shadowing effects, and impurities, as well as other imperfections in a material.

Patent publication WO 01/81649 A1 describes a method of depositing several thin ceramic barrier layers on top of each other on polymeric substrates to enhance the barrier abilities of the polymeric substrates. This publication suggests decoupling defects in successive ceramic barrier layers by changing the deposition parameters and growth conditions for the deposition of the ceramic barrier layers. According to the publication, this method should lead to mismatched subsequent barrier layers that exhibit different microstructures and therefore the paths for gases and water vapor permeation are degraded, leading to enhanced barrier abilities. Experiments carried out by the inventors indicate that ceramic barrier stacks produced by this method exhibit enhanced barrier abilities, but show no major improvements over applying a single ceramic barrier layer when defects larger than grain boundaries, e.g., pinholes or shadowing effects, are present.

SUMMARY

There is a need for polymeric substrates with improved barrier abilities. The present invention can meet these needs by forming an arrangement of barrier layers on a polymeric substrate.

Methods for forming an arrangement of two ceramic barrier layers on a polymeric substrate are described. In one implementation, the method includes applying a first barrier layer on a substrate. The surface of the first barrier layer is then modified to introduce new nucleation sites on the surface of the first layer. A second ceramic barrier layer is then formed on the first barrier layer using the new nucleation sites.

Aspects of the techniques described herein may include none, or one or more, of the following advantages. The new nucleation sites on the first barrier layer can serve as a starting point for the formation of the second ceramic barrier layer. Due to

thermodynamics, the second ceramic barrier layers can be formed on the first barrier layers without continuing all the defects, such as pinholes and grains, of the first layer throughout the barrier layer. At least two thermodynamically decoupled layers may be grown on top of each other with independent nucleation for each layer.

Using methods described herein changes the grain boundaries on the surface of the first ceramic barrier layer. Because the grain boundaries can be reproduced in the second layer if no new nucleation is introduced, then the defects may form a path for water and oxidizing agents to travel through the ceramic barrier layers. Introducing new nucleation sites can ensure that subsequent layers can be formed on a ceramic barrier layer independent from the morphology and the energetic conditions of the ceramic layer. The nucleation can be sensitive to the kinetic energy and mobility of the molecules on the surface of a layer on an atomic scale. An arrangement of at least two ceramic barrier layers on a polymeric substrate formed by the methods described herein may be less permeable for gases and liquids than barrier stacks produced by conventional methods.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A to 1C show one embodiment of the inventive method in a cross-sectional view.

Figure 2 shows a cross-section of an OLED device produced according to one embodiment of the method of the invention.

DETAILED DESCRIPTION

A method for forming an arrangement of two ceramic barrier layers on a polymeric substrate includes applying a first barrier layer on the substrate. The surface of the first barrier layer is then modified to introduce new nucleation sites on the surface of the first layer. A second ceramic barrier layer is then formed on the first barrier layer using the new nucleation sites.

The introduction of new nucleation sites on the surface of the first layer can be performed by chemical surface modification, mechanical surface modification or by the application of nucleation-promoting material on the surface of the first layer. The

chemical surface modification can be performed by saturating "dangling" unsaturated bonds on the surface of the first layer or by changing the lattice parameters of the surface of the first layer by, e.g., oxidation. Alternatively, or in addition, the chemical surface modification can include acid treatment, base treatment, water vapor treatment, plasma treatment or ozone treatment. These modification methods can change the surface and introduce new nucleation sites on the surface of the first layer very efficiently.

Modifying the surface mechanically can include ion-milling, nano-grinding, melting the surface with a laser-beam or tempering. During ion-milling, the surface of a barrier layer can be treated with ion beams, such as argon ion beams or oxygen ion beams, to change the topology of the surface. During nano-grinding, the surface of the barrier layer can be polished using abrasive particles sized in the nanometer range. Tempering includes curing barrier layer by applying temperatures higher than temperatures applied during the formation of the barrier layer and to at least a partial rearrangement of the crystal lattice of the surface of this layer. Melting the surface with a laser-beam involves melting areas of the first ceramic barrier layer to rearrange the crystal lattice.

The surface of the a ceramic barrier layer can also be doped with nucleation promoting materials. The materials can be selected to have a small critical nucleus. The critical nucleus can include a single atom or molecule. The critical nucleus denotes the minimum number of atoms or molecules required to form a stable grain. The nucleation promoting materials can be selected from a group of metals, metal nitrides, metal oxides, silicon, silicon nitride and silicon oxide. Specifically, nucleation promoting materials can be selected from tantalum, chromium, tungsten, molybdenum, niobium, titanium, tantalum nitride, titanium nitride, tantalum oxide and titanium oxide. These materials are able to serve as nucleation sites for the growth of the second ceramic barrier layer. The nucleation promoting materials do not have to build up a continuous layer on the surface of the ceramic barrier layer. The deposited amount of nucleation promoting material on the surface of the first layer can be below the mass needed to create a monomolecular layer, i.e., the surface of the ceramic barrier layer need only be doped with the nucleation promoting material.

In one implementation, a ceramic material that is selected from one or more materials of a metal, metal oxides, metal nitrides, metal oxynitrides, silicon, silicon oxides, silicon nitrides and silicon oxynitrides is used to form ceramic barrier layers. The metal for these metal nitrides, metal oxides or metal oxynitrides can be aluminum. These ceramic materials are able to serve as barrier layers that block out gases or liquids. Apart from these materials, other ceramic materials including predominately inorganic and non-metallic compounds or elements can be used. Each ceramic barrier layer can be of the same material. Alternatively, each ceramic barrier layer can include a different material than the other ceramic barrier layers.

Forming subsequent ceramic barrier layers can include deposition techniques, such as chemical vapor deposition (CVD) or physical vapor deposition (PVD). These methods can be used to deposit ceramic barrier layers of high quality on substrates.

The first barrier layer can be formed on a flexible, transparent substrate, e.g., polyethyleneterepthalate (PET). In one implementation, flexible, transparent substrates are used in organo-optical devices, such as the abovementioned OLEDs, because these substrates can be transparent to the light emitted by the OLEDs.

In one implementation, a third ceramic barrier layer is deposited on the surface of the second ceramic barrier layer by repeating the steps of introducing nucleation sites and forming a barrier layer using the new nucleation sites. In this implementation, the surface of the second ceramic barrier layer is also modified in order to introduce new nucleation sites. These new nucleation sites can serve as starting points for the deposition of the third ceramic barrier layer. An arrangement with three or more ceramic barrier layers can be used for applications where an extremely low permeation rate through the barrier layers for gases and liquids is necessary.

In forming the first, second and subsequent barrier layers, the barrier layers can have a thickness of about 1 to about 250 nm, such as a thickness of about 10 to 100 nm. Such thin layers can be used as barrier layers, for example, for transparent substrates on flexible OLED devices, because the light emitted by the OLED can pass through the thin barrier layers.

In one implementation, the arrangement of the ceramic barrier layers on the polymeric substrate produced by the methods described above can be used to build up

organic electrical devices, such as integrated plastic circuits or flexible organic light sensors such as organic solar cells or photodetectors. Therefore it is possible to form an organic functional layer after forming the second barrier layer. In this implementation, the arrangement of the substrate and the ceramic barrier layers can serve as a barrier stack to protect the sensitive organic functional layer from moisture or oxidizing agents.

In another implementation, subsequent steps of forming an OLED are performed. A first electrically conductive layer can be formed on the second barrier layer, and a functional organic layer can be formed on the first electrically conductive layer. A second electrically conductive layer can be formed on the functional organic layer. The conductive layers, which, for example, can comprise indium-tin oxide (ITO), can easily be patterned, e.g., to form stripes. The first electrically conductive layer can be patterned into a plurality of parallel electrode stripes, whereas the second electrically conductive layer can also be formed into a plurality of parallel electrode stripes running perpendicular to the electrode stripes of the first conductive layer. The crossing points between the electrode stripes of the first and of the second conductive layers can form pixels of the OLED device.

Furthermore, it is possible to form an encapsulation over an OLED device that is built up on a barrier arrangement. Encapsulation can include forming a fourth ceramic barrier layer over the second electrically conductive layer of the OLED device. The surface of the fourth barrier layer is subsequently modified to introduce new nucleation sites on the surface. Afterwards, a fifth ceramic barrier layer is formed on the fourth ceramic barrier layer. A similar encapsulation method can be use with other electrical devices

Figure 1A shows a first ceramic barrier layer 5 formed on a substrate 1. The arrows 2 denote the formation of the first ceramic barrier layer 5.

Figure 1B is a cross-sectional view of the substrate 1 with one barrier 5 layer having a modified surface 5A. The surface 5A of the first ceramic barrier layer 5 is modified by chemical or mechanical modification or by introduction of nucleation promoting material to introduce new nucleation sites. The arrows 3 denote the direction of the surface modification.

Figure 1C shows an arrangement of the substrate 1, the first ceramic barrier layer 5 and the second ceramic barrier layer 10 after depositing the second barrier layer 10. The second ceramic barrier layer 10 is deposited on the modified surface 5A of the first ceramic barrier layer 5. The new nucleation sites of the surface 5A cause the first barrier layer to have a different morphology in the areas of the first ceramic barrier layer 5 that are located below the surface 5A as the corresponding portions of the surface. The second layer 10 can be grown on the first ceramic barrier layer with independent nucleation and different grain boundaries.

Figure 2 is a cross-sectional view of an OLED device formed by methods described herein. The electrical functional stack of the OLED device has at least one organic functional layer 20 inserted between a first electrically conductive layer 15 and a second electrically conductive layer 25. The electrical, functional stack is formed on a barrier arrangement consisting of the polymeric substrate 1, the first ceramic barrier layer 5 and the second ceramic barrier layer 10, which is deposited on the modified surface 5A of the first ceramic barrier layer using new nucleation sites. An encapsulation 40 consisting of the third ceramic barrier layer 30 and the fourth ceramic barrier layer 35 is formed on top of the electrical, functional stack of the OLED device, sealing the electrical, functional stack of the device from the environment. The surface 30A of the third ceramic barrier layer 30 includes the nucleation sites for forming the fourth ceramic barrier layer 40. Contact pads 50, 60, which are connected to the first 15 and the second electrically conductive layer 25 are present to enable an electrical connection to the OLED. Therefore, the methods described above can provide an OLED device with enhanced lifetime and can be formed with a tight encapsulation.